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Water Gas Shift Reaction Catalyzed by Osmium Carbonyls Supported on Zeolites

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The kinetics of the water gas shift reaction (WGSR) ($CO + H_2O \rightleftarrows CO_2 + H_2$) catalyzed by osmium carbonyls supported on X-type zeolite have been studied using a flow reactor. The influence of water content and CO pressure have been examined at varying temperatures. Evidence for water activation by the surface of the zeolite and an inhibition effect at higher CO pressure have been found. The nature of the carbonylic surface species and their interconversion have been studied by spectroscopic techniques.

INTRODUCTION

The water gas shift reaction (WGSR) is widely used to increase the hydrogen content of synthesis gas through the reaction of steam with carbon monoxide. Catalysts currently active at temperatures lower than that used in the industrial process are still of interest as a result of a more favorable thermodynamic equilibrium (*1*).

The reaction has been studied in the homogeneous phase by several research groups (see, for example, Refs. (*2–4*)), generally in basic media, using transition metal carbonyls as catalyst precursors. In basic media the carbonyl clusters of many transition metals generate a mixture of carbonyl anions and/or carbonyl hydrides, which appear to be the active species in the catalytic process. The activity is in general rather poor and not competitive with that of the commercial copper-based low-temperature shift catalyst.

Over the last decade there has been growing interest in the use of catalytic systems formed by supporting transition metal complexes and carbonyl clusters on inorganic oxides or zeolites (*5–12*). Transition metal ions exchanged on zeolites have been widely studied, to clarify the reaction mechanism and/or to characterize the active surface carbonylic species (*5–9*). Studies of the catalytic behavior in the WGSR of transition metal carbonyl clusters supported on inorganic oxides are limited to rhodium clusters (*12–14*) on alumina and zeolites, although indications of potential activity in the WGSR of transition metal clusters supported on various oxides can be found in the literature (*15*).

In recent years we have studied the WGSR using the osmium cluster $Os_3(CO)_{12}$ supported on the acid form of a 13X zeolite as catalyst precursor (*10, 11*). To obtain a better understanding of the nature of the active species involved in the catalytic cycle and on the mechanism of the reaction we have undertaken a kinetic study of the WGSR in a flow reactor and a more detailed investigation on the nature of the various species which are formed on the zeolitic surface.

EXPERIMENTAL

Materials and Catalyst Preparation

$Os_3(CO)_{12}$ was obtained from Strem and used without further purification. The gases, obtained from SIAD, had purities of 99.9%. The sodium form of 13X zeolite was obtained from Linde and used without any

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chemical treatment but was ground to 60–100 or 20–40 mesh. The acid form was prepared by conventional methods. $Os_3(CO)_{12}$ was physisorbed on the zeolite as previously described (*10*). The species Os-1(G), Os-2, Os-3 were routinely prepared as follows.

Os-1(G). A solution of $Os_3(CO)_{12}$ (100 mg) in *n*-octane was refluxed with 4 g of HX zeolite under N_2 atmosphere. The reaction was completed in 24 h, when the initially yellow solution became colorless. A metal loading of 1.6% by weight was obtained. IR stretching frequencies in the ν_{CO} region were observed at 2132, 2075, 2063, and 2022 cm^{-1}.

Os-2. Os-1(G) was heated for 4 h at 140°C in CO atmosphere. The compound was stable in CO atmosphere up to 270°C (ν_{CO} = 2132, 2046 cm^{-1}).

Os-3. This species was prepared by heating Os-1(G) in O_2 atmosphere for 3 h at 140°C (ν_{CO} = 2128, 2045, and 1960 cm^{-1}).

Regeneration of Os-2 from Os-3. A self-supporting wafer of zeolite containing Os-3 was heated in an evacuable IR cell (*12, 16*) for 30 min at 200°C in CO atmosphere (100 kPa). The cell was then evacuated to release the water trapped by the zeolite. Carbon monoxide was admitted to the system, and formation of Os-2 then took place at 200°C in 1 h.

Breakdown of Os-3-containing zeolite. The osmium-loaded zeolite (8 g, 1.6 wt% Os) suspended in 30 ml of distilled water was stirred in a Teflon beaker at room temperature; concentrated HF was added in small portions (0.5 ml at a time) until the solution remained acid. The reaction was complete after 24 h. All the volatile products were evaporated at 150°C in a graphite oven. The residue was extracted in a Soxhlet apparatus with EtOH (or MeOH) to give a pale yellow solution. Alcohol was evaporated giving a dark sticky oil which was purified by elution through a Florisil column to give a pale yellow oil (ν_{CO} = 2124, 2036, 1936 cm^{-1}, Nujol mull).

Spectroscopic Measurements and Analysis

The IR spectra were obtained as follows. Powders of the catalyst material were pressed into self-supporting wafers at a pressure $\cong 6 \times 10^3$ kPa and were mounted in a conventional holder or in an evacuable IR cell (*12, 16*). Spectra were recorded on a Perkin–Elmer 983 instrument equipped with a Perkin–Elmer Data Station 3600. Atomic absorption measurements were made with a Perkin–Elmer 4000 instrument. UV spectra were measured on a Perkin–Elmer Lambda 5 UV spectrometer in the region 250–600 nm ($CHCl_3$ solution). Mass spectrometric measurements were performed on YG ZAB2F and VG micromass 70/70 instruments operating under electron impact conditions (70 or 20 eV, 200 μA). Samples were introduced under direct electron impact (DEI) conditions with a source temperature of 100–200°C (*17*). Some experiments were carried out under chemical ionization conditions using CH_4 and NH_3.

Catalytic Measurements

The catalytic experiments were carried out in a tubular (23-cm-length × 9.5-mm-o.d.) stainless-steel flow reactor interfaced to a gas–liquid chromatograph. Water was vaporized into the stream of carrier gas (argon) using a thermostated saturator. The kinetic measurements were performed under differential conditions (conversion <5%). In a typical experiment, 3 g of Os-1(G) (20–40 mesh) was placed between two layers of granular quartz; then the system was deaerated with flowing argon for 12 h at room temperature. The catalyst was activated at 180°C at a total feed of 6.4 ml/min (P_{H_2O} = P_{CO} = 12.6 kPa) for 4 h. During this time Os-2 was formed, and the steady-state conditions were attained after a further 2 h of reaction. The analyses of the reactants and the products in the gas phase were performed on a DANI 3400 gas chromatograph

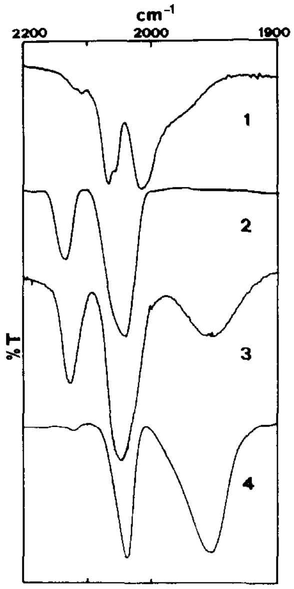


FIG. 1. IR spectra in the ν(CO) region of: (1) $Os_3(CO)_{10}$ (μ–H) (μ–O–surface) (ν = 2132, 2075, 2063, 2022 cm^{-1}); (2) Os-2 (ν = 2132, 2046 cm^{-1}); (3) Os-3 (ν = 2128, 2045, 1960 cm^{-1}); (4) Os-2B (ν = 2043, 1958 cm^{-1}).

equipped with a TC detector, using a 2-m molecular sieve 5-Å column or a 5-m Porapak Q column and argon as carrier gas.

RESULTS AND DISCUSSION

$Os_3(CO)_{12}$ was adsorbed on an acid zeolite (HX) prepared from a commercial 13X zeolite by conventional methods, to give [$Os_3(CO)_{12}$–HX]. The adsorbed cluster generates, by thermal treatment (*10*), a carbonyl species which appears to be the grafted cluster [$HOs_3(CO)_{10}$–O–surface], henceforth indicated as Os-1(G) (Fig. 1, spectrum 1), similar to the osmium species reported to form on inorganic oxides (*15*, *18*).

This species catalyzes the WGSR at temperatures >140°C under batch conditions (*10*) under 100 kPa of carbon monoxide, in the presence of an excess of water. In preliminary work (*10*) it was observed that the grafted species Os-1(G) evolves during the reaction to a different carbonyl species, hereinafter indicated as Os-2 (Fig. 1, spectrum 2), with two IR bands at 2132 and 2046 cm^{-1} in the ν(CO) region. This species shows constant catalytic activity in the WGSR and it appears firmly bonded to the surface. In the absence of carbon monoxide Os-2 transforms into another species, designated as Os-3, with IR bands in the ν(CO) region at 2128, 2045, and 1960 cm^{-1} (Fig. 1, spectrum 3) which catalyzes the WGSR under static conditions to a lesser extent (turnover number TN = 5.5 compared to TN = 12 obtained with Os-2, where TN = mol CO_2 · metal atoms^{-1} · day^{-1}) (*10*).

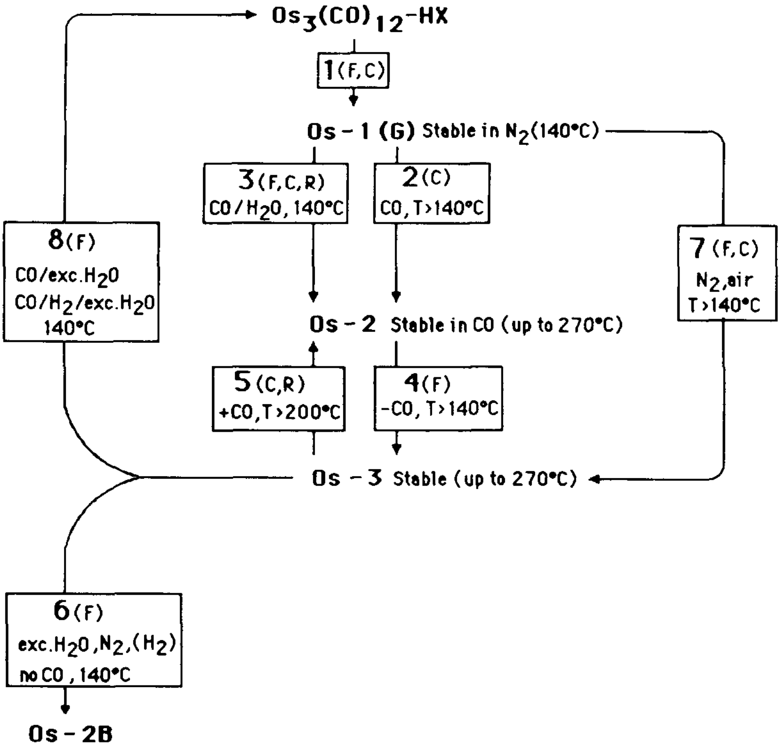
Consequently we decided to undertake a more detailed study with a view to clarifying the nature of the Os-2 and Os-3 species.

Catalyst Characterization

Scheme 1 summarizes the behavior of the various species generated by $Os_3(CO)_{12}$ supported on the X-type zeolite. Experiments have been performed in an IR cell (Scheme 1, C), in a glass reaction flask (Scheme 1, F) and in a batch or flow reactor (Scheme 1, R). The triosmium cluster Os-1(G), grafted to the surface, generates the carbonyl Os-2 in the presence of CO at temperatures >140°C or under WGSR conditions at 140°C (Scheme 1, paths **2** and **3**).

The Os-2 carbonyl is stable in the presence of CO up to 270°C, but in the absence of CO, at temperatures >140°C, it evolves into the Os-3 species (Scheme 1, path **4**). Os-3 is stable up to 270°C, but in the presence of added water and in the absence of CO (N_2 or H_2 atmosphere) it transforms into a different species, designated further as Os-2B, with IR bands at 2043 and 1958 cm^{-1} (Fig. 1, spectrum 4; Scheme 1, path **6**).

A species with an IR spectrum similar to that of Os-2B has been previously observed (*11*) in studying the WGSR catalyzed by $Os_3(CO)_{12}$ on 13X zeolite in the presence of bases. The Os-3 species can also be generated from the grafted cluster Os-1(G) by thermal treatment in the absence of CO, at



SCHEME 1. Species formed from $Os_3(CO)_{12}$ supported on HX zeolite.

temperatures >140°C (Scheme 1, path **7**). Os-3 can generate Os-2 by thermal treatment ($T > 200$°C) in the presence of CO (see under Experimental) (Scheme 1, path **5**).

These experiments show quite clearly that the grafted cluster Os-1(G) undergoes a series of thermal transformations giving the active species Os-2, stable in the presence of CO and Os-3 which forms in the absence of CO. The spectroscopic characterization of these species is complicated by the breadth of the IR bands and by the fact that the Os-3 spectrum in the carbonyl region seems to be a combination of Os-2 and Os-2B spectra (Fig. 1, spectra 2–4).

Further experiments, however, support the presence of three individual species. Os-2B does not regenerate Os-3, but under certain conditions Os-2 is obtained from Os-3 (Scheme 1, path **5**).

The nature of the surface species formed by thermal decomposition of osmium clusters on various oxides has been widely investigated and spectra very similar to those of Os-2 and Os-3 have been found (*15, 18–25*). Osmium clusters such as $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, and $H_4Os_4(CO)_{12}$, impregnated on silica, alumina, or titania, heated up to 250°C, give surface products with IR spectra similar to those of Os-3. The products were described on the basis of diffuse reflectance UV spectra as a family of high-nuclearity clusters (*23, 24*).

Species with similar spectra have been described as $[Os(CO)_3]_n$ and $[Os(CO)_2]_n$ oligomers ($n > 2$) bonded to the surface. This attribution was supported mainly by isotope labelling IR measurements (*25*). Recently the species formed by $Os_3(CO)_{12}$ on γ-alumina has been studied by EXAFS (*26*). After thermal treatment in a helium stream at 150°C, the Os–Os signal disappears suggesting the formation of mononuclear oxidized osmium carbonyl species bonded to the support by three oxygen atom neighbors. Therefore the validity of the mixed valence macrocluster hypothesis seem to be confined to those particular experimental conditions (*23, 24*).

By comparison of the IR spectra of the surface carbonyls formed on alumina by thermal treatment of $Os_3(CO)_{12}$ with model compounds, the formation of mononuclear oxidized species of the type $>Os(CO)_x$ ($x = 2, 3$) has been suggested (*15*). Successive careful analysis of the IR spectra suggested $x = 2$ for the species with bands at 2130 and 2040 cm^{-1} and $x = 3$ for the species with bands at 2040 and 1970 cm^{-1}, the spectrum with three bands belonging to a mixture of the two (*20, 21*). Nevertheless, the exact nature of the species produced on the surface by thermal degradation of the osmium cluster still remains to prompt open questions as follows. (a) Are we in the presence of individual species or a mixture of carbonyls? (b) How many carbonyl groups are bonded to the osmium centers?

In order to obtain more information on the nature of these surface species we extracted the Os-3 from the zeolite broken down with hydrofluoric acid. We obtained a pale yellow oil not containing Si and Al as proved by atomic absorption spectroscopy. The IR spectrum in the ν(CO) region of this compound presents the same pattern and the same relative intensities as those of the surface species Os-3 even though after the extraction a small shift of the IR bands in the ν(CO) region is observed (Fig. 2, spectra 1–3). In the high-frequency region no bands are present besides the ν(CO) absorption at 2200–1900 cm^{-1}. In the low-frequency region (800–180 cm^{-1}, Fig. 2, spectrum 4) several medium intensity bands are present which, consistent with our hypothesis on the nature of this species, (see

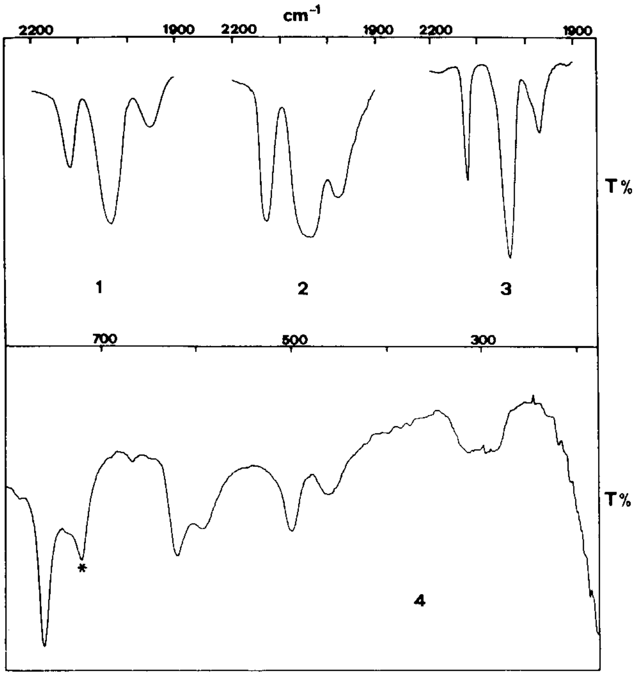


FIG. 2. IR spectra in the ν(CO) region (**1–3**) and in the δ(Os–CO), ν(Os–C), and δ(O–Os–O) (**4**) of: (1) Os-3 supported on HX zeolite (ν = 2128, 2045, 1960 cm^{-1}); (2) Os-3 extracted from the HX zeolite in Nujol mull (ν = 2124, 2036, 1976 cm^{-1}); (3) Os-3 extracted from the HX zeolite in $CHCl_3$ solution (ν = 2123, 2038, 1972 cm^{-1}); (4) Os-3 extracted from the HX zeolite in Nujol mull (ν = 762, 669, 622, 596, 502, 464, 318, 292 cm^{-1}); *Nujol.

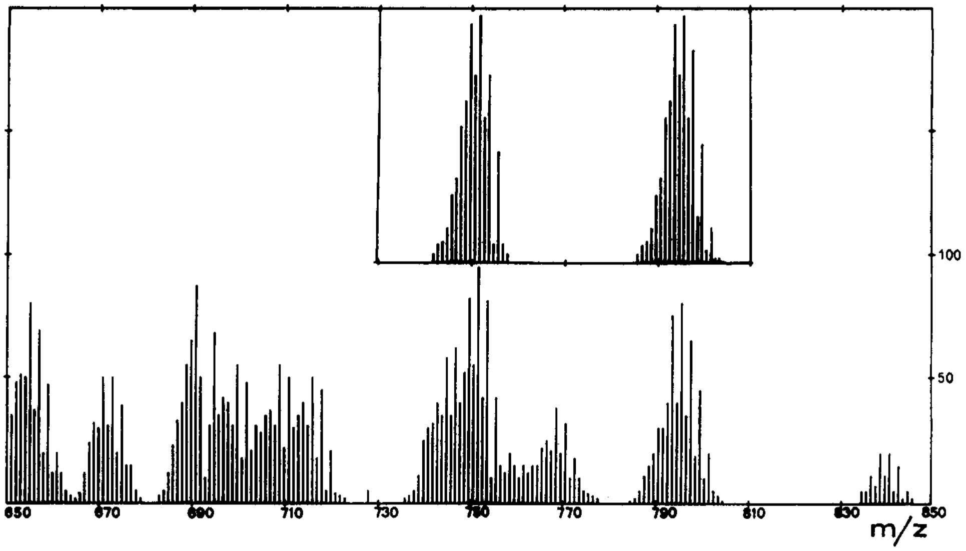
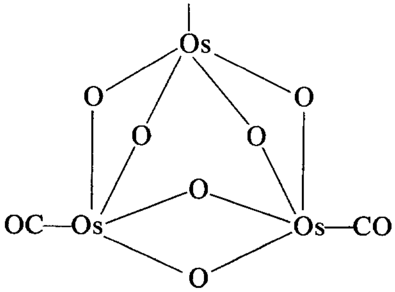


FIG. 3. Mass spectrum of Os-3 extracted from the zeolite. In the inset the theoretical isotopic clusters of $C_3O_9Os_3$ (*m/z* 750) and $C_4O_{11}Os_3$ (*m/z* 796) are represented.

later), are attributable to δ(Os–C–O), ν(Os–C) (800–400 cm^{-1}), and δ(O–Os–O) (400–200 cm^{-1}) (*27*).

The compound examined by mass spectrometry under EI or CI (CH_4, NH_3) conditions shows a set of isotopic clusters in the mass range 650–850 (Fig. 3). The most abundant peaks in the mass spectrum are around *m/z* 796 and 750. The former fits with the theoretical isotopic cluster due to a $C_3O_9Os_3$ moiety (Fig. 3). The complete lack of EL-induced fragmentation products related to monometallic or bimetallic moieties strongly suggests the presence of cyclic precursors. Therefore we suggest a structure of type **a** for the $C_3O_9Os_3$ moiety.



a

The absence of osmium–osmium bonds in the ion **a** is confirmed, by the UV spectrum of the original sample which consistently shows no absorption peaks in the region 250–640 nm attributable (*28*) to osmium–osmium bonds.

Ionic species at *m/z* 722 (Fig. 3) can be easily explained by a primary CO loss from the ion **a**, while the isotopic cluster analysis (Fig. 3) gives an elemental composition of $C_4O_{11}Os_3$ for the ion at *m/z* 796. For this species a cyclic structure with one more oxygen bridge and one of the osmium atoms bearing two carbonyl groups can be suggested.

This fragmentation pattern, together with all the other spectroscopic evidence, strongly supports in our opinion the presence on the surface of mononuclear dicarbonyl species of the type $\diagdown Os(CO)_2$. Therefore the Os-2 species, which is formed by carbonylation of Os-3 (Scheme 1, path **5**), should be a species of the type Os$(CO)_3$.

We think that the thermal oxidation–decarbonylation process of the osmium cluster on the surface generates mononuclear carbonyls strongly bonded to the oxygen atoms of the surface with a structure reminiscent of the cluster skeleton because of formation of strong Os–O bonds which is probably the driving force of the process (*20*). The idea of a similar decomposition with formation of ensembles of three osmium atoms was suggested some years ago (*20, 29*) to explain the presence of small scattering centers observed by electron microscopy on samples produced by thermal decomposition of $Os_3(CO)_{12}$ physisorbed on alumina.

The water content in the zeolite seems to play an important role in the evolution of the surface species. The grafted cluster Os-1(G) loses its nuclearity via oxidative addition of surface OH groups (or zeolitic water) to generate the Os-2 species, stable under CO atmosphere (Scheme 1, path **2**). The presence of carbon monoxide in this process is necessary to stabilize Os-2 and to avoid Os-3 formation (Scheme 1, path **7**).

Path **4** of Scheme 1 (i.e., Os-3 formation from Os-2) appears to be a hydrothermal process, since the Os-2 species is more easily reformed if water is pumped off at 200°C (see under Experimental) before the CO is readmitted. This behavior is consistent with a competitive coordination of CO and H_2O (or OH^-) toward the same coordination sites on the Os-3 species. The Os-3 species regenerates $Os_3(CO)_{12}$ when treated with CO and H_2 in the presence of a large excess of H_2O (1 : 1 : 20 molar ratio) at 140°C (Scheme 1, path **8**). The cluster can be recovered by sublimation or extraction. Addition of H_2 is not necessary, since it is produced via WGSR; when added, however, it shortens the reaction time (24 h instead of 100 h). Hydrolysis of the metal–surface bond and subsequent reductive carbonylation, facilitated by the presence of the ensembles of osmium atoms (*20, 29*), give a possible explanation for this reaction which seems not to have a homogeneous counterpart.

It is worth mentioning that when a large excess of propanol is used in place of water, $[HOs_3(CO)_{10}(OR)]$ is obtained, probably via reaction of ROH with $Os_3(CO)_{12}$ formed in the first step of reaction.

Spectroscopic evidence for the formation of cluster species from metal carbonyls on the surface in the presence of CO and water has been observed in some cases. Thus, the surface carbonyl "$Rh(CO)_2$" on silica and alumina (*30*) or zeolite (*31*) regenerates $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. A similar reaction occurs in solution (*32*). The reaction of the osmium covalently grafted cluster $[HOs_3(CO)_{10}(O{-}Si{\leqq})]$ on silica, with water and carbon monoxide, is outlined by Psaro *et al.* (*15*) to obtain $Os_3(CO)_{12}$. Such a reaction also occurs with the grafted cluster $[HRu_3(CO)_{10}(O{-}Si{\leqq})]$ (*33*). In this work, the regeneration of $Ru_3(CO)_{12}$ from oxidized $Ru^{II}(CO)_n(O{-}Si{\leqq})$ (n = 2, 3) carbonyl in the presence of water and carbon monoxide was reported as well.

Reactivity under Flow Conditions

The Os-1(G) grafted cluster has also been tested in a flow reactor operating at atmospheric pressure under differential conditions.

Also under these conditions an evolution of the catalyst was observed. After 4 h at 180°C on stream ($P_{CO} = P_{H_2O} = 12.6$ kPa, total feed 6.4 ml/min), the species Os-2 is formed from the grafted cluster Os-1(G) (the catalyst extracted from the reactor showed the typical IR spectrum with the two broad bands at 2132 and 2046 cm^{-1}). This species is stable for weeks under the flow conditions as long as CO is present.

We examined the catalytic activity of Os-2 in the temperature range 205–265°C and in the pressure range 4–75 kPa of CO and H_2O. The apparent activation energy was 74 ± 6 kJ/mol, which is close to the value of 65 kJ/mol reported for the system $Rh_6(CO)_{16}$/alumina (*12*).

The reaction rate, at 205°C, showed a typical Langmuir-type dependence on the water pressure (Fig. 4, curve A). Zero-order dependence was observed at pressures higher than 27 kPa. At 265°C (Fig. 4, curve C) the plateau was not reached, probably

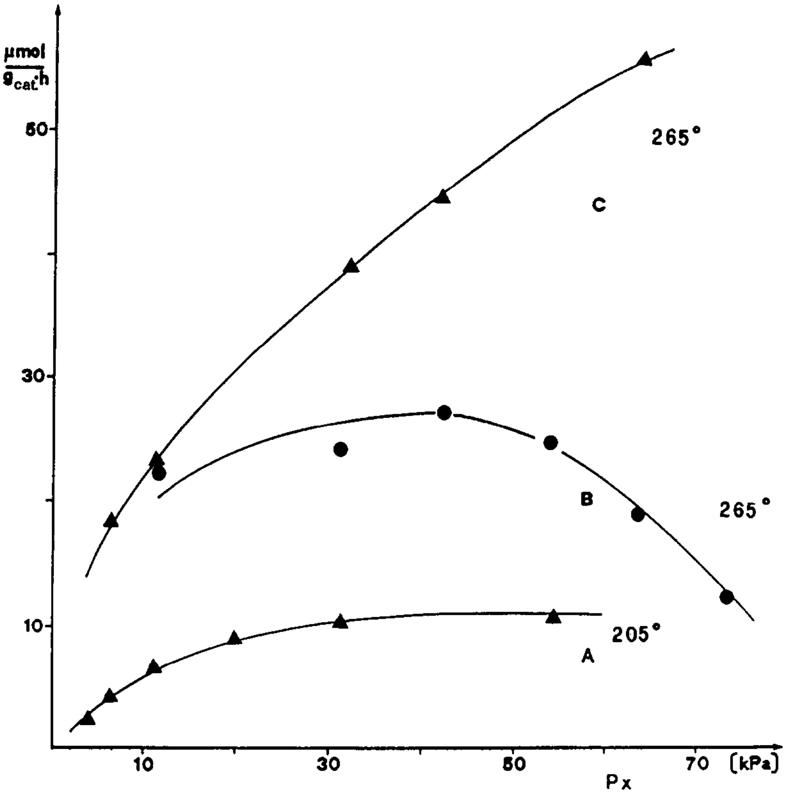


FIG. 4. Reaction rate dependence on P_{H_2O} and P_{CO}. (▲) $X = H_2O$, curves A and C; (●) $X = CO$, curve B.

because of the competing thermal dehydration of the zeolite.

These observations indicate that the water molecules are strongly chemisorbed by the support before they react with the supported osmium carbonyl. Water chemisorption on the support can occur dissociatively, nondissociatively, or both (*6*). Under our experimental conditions, using an acid zeolite and relatively low reaction temperatures, the nondissociative absorption is likely to be the prevalent mechanism for water activation. Therefore the following equilibrium can be written for this process:

$$H_2O + S \underset{}{\overset{K_1}{\rightleftarrows}} H_2O{-}S \qquad (1)$$

where S indicates the support.

The dependence on CO pressure at $P_{H_2O} = 11$ kPa is reported in Fig. 4, curve B. At low CO pressures ($P_{CO} \leq 50$ kPa), small changes in the reaction order are observed while higher pressures of CO slow down the reaction rate.

It is generally assumed that in an acidic medium the WGSR proceeds through the nucleophilic attack of a water molecule on CO coordinated to the metal center with formation of a formate intermediate (*2*). A higher oxidation state of the metal favors the nucleophilic attack of the water molecule and this can account for the extremely low catalytic activity of the species Os-2B (*11*). This last species is probably a reduced form of the surface carbonyl $>Os(CO)_2$ (*20*). This assumption is supported by the generally reducing conditions (CO/KOH) (*11*) that favor its formation. Therefore the reaction can proceed via nucleophilic attack of the activated water molecule on the

Os-2 species with formation of a formate complex. The presence of formate intermediate has been observed in several cases (*5, 6, 34*) but we have not detected any absorption in IR spectra attributable to the formate ion because of the obscuring effect of the support. Nevertheless, formic acid is decomposed by our catalyst. Consequently, the following equilibrium can reasonably account for the formation of the formate species:

$$>\mathrm{Os(CO)_3} + \mathrm{H_2O{-}S} \overset{K_2}{\rightleftarrows} >\mathrm{Os(CO)(CO_2H)(H)} + \mathrm{CO} \qquad (2)$$

The formation of the formate complex requires a free coordination site. The CO dissociation in this step can create the coordination vacancy on the metal center and at the same time it accounts for the inhibiting effect of CO.

Recently, an EXAFS investigation of the oxidized osmium carbonyl species supported on alumina has suggested the presence of three oxygen atoms in the coordination sphere of the osmium atom (*26*), and this result could also support the CO dissociation we invoke in the equilibrium (2).

The decomposition of the formate complex proceeds with the evolution of CO_2 and formation of a metallic hydride:

$$>\mathrm{Os(CO)(CO_2H)(H)} \xrightarrow{k_3} >\mathrm{Os(CO)(H)(H)} + \mathrm{CO_2} \qquad (3)$$

The reductive elimination of H_2 was proposed as the rate-determining step for the homogeneously catalyzed WGSR in acidic media (*2*).

In our case, the H_2 evolution from the hydride species should lead to the formation of a highly reactive osmium monocarbonyl species, which should then be rapidly recarbonylated to give an $>Os(CO)_2$ species. Notably, when such a hypothesis is considered, upon application of the steady-state approximation and assuming a Langmuir-type adsorption for the water activation, a kinetic equation at constant H_2O pressure of the type

$$r = \frac{k_a P_{\mathrm{CO}}}{1 + k_b P_{\mathrm{CO}}}$$

is obtained. This equation, however, does not account for the experimental data.

Consequently a CO-assisted H_2 evolution can be proposed:

$$>\mathrm{Os(CO)(H)(H)} + \mathrm{CO} \xrightarrow{k_4} >\mathrm{Os(CO)_2} + \mathrm{H_2} \qquad (4)$$

which gives the species $>Os(CO)_2$ which is then recarbonylated according to the equilibrium

$$>\mathrm{Os(CO)_2} + \mathrm{CO} \overset{K_5}{\rightleftarrows} >\mathrm{Os(CO)_3} \qquad (5)$$

The rate-determining step of the overall reaction could be either the decomposition of the formate intermediate (Eq. (3)) or the H_2 evolution (Eq. (4)). In the first case, the following rate equation can be obtained:

$$r = k_3 C_{\mathrm{A}}, \qquad (6)$$

where C_A denotes the concentration of the $>Os(CO)(CO_2H)(H)$ sites and k_3 is the kinetic constant.

The total concentration of metal sites is

$$C_{\mathrm{Os(TOT)}} = C_{\mathrm{Os(CO)_3}} + C_{\mathrm{Os(CO)_2}} + C_{\mathrm{A}} + C_{\mathrm{B}}, \qquad (7)$$

where $C_{Os(CO)_3}$, $C_{Os(CO)_2}$, C_B denote the concentrations of the species $>Os(CO)_3$, $>Os(CO)_2$, and $>Os(CO)(H)(H)$, respectively.

Dividing Eq. (6) by Eq. (7) we obtain

$$\frac{r}{C_{\mathrm{Os(TOT)}}} = \frac{k_3 C_{\mathrm{A}}}{C_{\mathrm{Os(CO)_3}} + C_{\mathrm{Os(CO)_2}} + C_{\mathrm{A}} + C_{\mathrm{B}}}. \qquad (8)$$

Substituting into Eq. (8) the values of $C_{Os(CO)_3}$, $C_{Os(CO)_2}$ and C_A obtained from equilibria (1), (2), (5) and assuming the steady-state approximation to be valid for the species $>Os(CO)(H)(H)$,

$$\frac{dC_{\mathrm{B}}}{dt} = k_3 C_{\mathrm{A}} - k_4 C_{\mathrm{B}} P_{\mathrm{CO}} = 0,$$

we finally obtain the rate equation

$$r = \frac{k_3k_4K_1K_2K_5P_{H_2O}P_{CO}C_{Os(TOT)}}{K_1K_2K_5P_{H_2O}(k_3 + k_4P_{CO}) + k_4P_{CO}(1 + K_5P_{CO})(1 + K_1P_{H_2O})}. \tag{9}$$

At constant $P_{CO} = 11$ kPa, this equation can be simplified to

$$r = \frac{k_aP_{H_2O}}{1 + k_bP_{H_2O}}. \tag{10}$$

Equation (10) accounts for the catalytic behavior of the system at constant CO pressure, and while operating at constant H_2O pressure Eq. (9) simplifies to

$$r = \frac{k_cP_{CO}}{1 + k_dP_{CO} + k_eP_{CO}^2} \tag{11}$$

which also accounts for the experimental data.

Notably when hydrogen evolution (Eq. (4)) is assumed as the rate-determining step, a rate equation at constant P_{H_2O} of the type $k_aP_{CO}/(1 + k_bP_{CO})$ is obtained which does not account for the experimental data.

We also tested the Os-3 species in the flow reactor. However, during this experiment, the species Os-3 slowly transforms into the Os-2 carbonyl as the intensity of the IR band at 1960 cm^{-1} decreases (Scheme 1, path **5**). Therefore the experimental data were not kinetically significant.

CONCLUSIONS

The reaction of $Os_3(CO)_{12}$ with the surface of a 13X zeolite in acid form leads initially to the formation of the grafted cluster Os-1(G).

By thermal and/or chemical treatments of the Os-1(G), degradation products are formed which appear to be formally oxidized di- and tricarbonyl mononuclear osmium carbonyls. Mass, UV, and IR spectra of the osmium carbonyl extracted from the zeolite strongly suggest the presence of mononuclear carbonyls bonded to the oxygen atoms of the surface with a structure reminiscent of the cluster skeleton. These data confirm the hypothesis of formation of ensembles of three osmium atoms on thermal degradation of chemisorbed $Os_3(CO)_{12}$ (*20, 29*).

Kinetic data confirm the importance of the zeolitic framework in the activation of the water molecule toward the nucleophilic attack on the coordinated carbon monoxide. Decomposition of an intermediate formate adduct is suggested to be the rate-determining step of the catalytic reaction.

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